

# First Principles Investigation of Hydrogen Physical Adsorption on Graphynes' layers

Massimiliano Bartolomei\* and Estela Carmona-Novillo

*Instituto de Física Fundamental, Consejo Superior de Investigaciones  
Científicas (IFF-CSIC), Serrano 123, 28006 Madrid, Spain*

Giacomo Giorgi

*Department of Chemical System Engineering,  
School of Engineering, University of Tokyo, Tokyo, Japan*

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Graphynes are 2D porous structures deriving from graphene featuring triangular and regularly distributed subnanometer pores, which may be exploited to host small gaseous species. First principles adsorption energies of molecular hydrogen ( $H_2$ ) on graphene, graphdiyne and graphtriyne molecular prototypes are obtained at the MP2C level of theory. First, a single layer is investigated and it is found that graphynes are more suited than graphene for  $H_2$  physical adsorption since they provide larger binding energies at equilibrium distances much closer to the 2D plane. In particular, for graphtriyne a flat minimum located right in the geometric center of the pore is identified. A novel graphite composed of graphtriyne stacked sheets is then proposed and an estimation of its 3D arrangement is obtained at the DFT level of theory. In contrast to pristine graphite this new carbon material allow both  $H_2$  intercalation and out-of-plane diffusion by exploiting the larger volume provided by its nanopores. Related  $H_2$  binding energies for intercalation and in-pore adsorption are around 0.1 eV and they could lead to high storage capacities. The proposed carbon-based layered material could represent a safer and potentially cheaper alternative for hydrogen on-board storage than conventional solutions based on cryogenic liquefaction and/or high compression.

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## I. INTRODUCTION

Hydrogen is a clean-burning energy carrier which is supposed to provide the most promising alternative to fossil fuels to be employed in propulsion systems for automotive applications. However, some drawbacks such as the safe and convenient hydrogen storage[1] and release in reversible cycles still represent major challenges to the scientific community. The use of advanced solid state adsorbents has recently received wide attention since they could provide solutions to achieve the 2017 targets for on-board vehicle hydrogen storage established by the U.S. Department of Energy (DOE): they are actually 5.5 wt% and 0.040 kg L<sup>-1</sup> for gravimetric and volumetric capacities, respectively[2], and they have not been simultaneously reached yet in practice at moderate temperature and pressure.

As a matter of fact, the physisorption of molecular hydrogen (H<sub>2</sub>) in porous materials represents a safer, simpler and potentially cheaper option for gas storage than conventional solutions, based on liquefaction at low temperature (and/or high compression at room temperature). Materials traditionally used in these applications include activated carbons and zeolites and in recent years novel and promising adsorbents, namely metal-organic frameworks (MOF) and covalent organic frameworks (COF)[3], are also available. MOF and COF possess advantages with respect to traditional porous materials due to their crystalline structure: in fact, their regular and ordered porosity, together with tunable size and shape of the openings, has led to very high performances in gas uptake capacities[4]. However, they present some shortcomings mainly related to their thermal and chemical stability. Moreover, the presence of heavy metals in MOFs, which in general enhances the binding strength of a given adsorbate, could also induce its dissociation which would alter the desirable gas storage and delivery reversible cycle. Therefore, investigations on alternative porous materials are highly advisable and, specifically, we here focus on carbon-based layers, which in general provide a large specific surface area coupled with a lower weight.

In the last years, by following “bottom-up” assembly processes two-dimensional (2D)

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\*Electronic address: maxbart@iff.csic.es

materials similar to ubiquitous graphene but with regular and uniformly distributed sub-nanometer pores have been synthesized in large area films[5, 6], and among them graphdiyne is of particularly interest for our purposes. Graphdiyne is actually a member of  $\gamma$ -graphynes which are new 2D carbon allotropes formed by sp-sp<sup>2</sup> hybridized carbon atoms. They can be thought as deriving from graphene by replacing one-third of its C-C bonds with mono(poly)-acetylenic units. The number  $n$  of acetylenic linkages which connect the benzene rings defines the different graphyne- $n$  species and the first three members of the family are known as graphyne, graphdiyne and graphtriyne, respectively[7], and they feature nanopores of increasing size. The successful synthesis of graphynes has led to important theoretical studies devoted to their application as effective single-layer membranes for gas separation and water filtration technologies[8–11].

In this work we want to assess the capability of graphynes as efficient materials for the reversible storage of molecular hydrogen and a fundamental point is to address the possibility of gas adsorption by exploiting its intercalation. As it is well known intercalation of gases between pristine graphene layers it is not feasible since large values of the interlayer distance would be needed for an effective storing[12, 13] (roughly the double with respect to graphite equilibrium distance). This requirement is difficult to fulfill in practice since it depends on an “a priori” forced separation of the graphene layers. On the contrary novel graphites composed of multi-layer graphynes could allow intercalation without significantly altering the interlayer separation since a larger available volume is in principle provided by the naturally occurring nano-pores.

The interaction of nonpolar H<sub>2</sub> molecules with carbon-based substrates is mainly the London dispersion and expected values for its binding energy with a single(multi)-layer are around 50 meV[14–16]. The H<sub>2</sub>–graphdiyne single-layer interaction was previously theoretically investigated[8, 17] by means of dispersion-corrected density functional theory (DFT) approaches but the focus was mostly on the penetration barrier in order to propose graphdiyne as an optimal platform for hydrogen purification. The three-dimensional (3D) diffusion of H<sub>2</sub> in bulk graphdiyne was also recently investigated[18] but the obtained dispersion-corrected DFT interaction energies were unreasonably too high with binding energies larger than 400 meV. More accurate estimations for the noncovalent H<sub>2</sub>–graphynes interaction are therefore desirable and their calculations would require reliable computational approaches. Our choice is to use the “coupled” supermolecular second-order Møller-Plesset

perturbation theory (MP2C) which has been reported to provide reliable estimations for weakly bound systems such as rare gas–fullerene[19] and -coronene[20] as well as water(rare gas)–graphynes’ pores[10, 11].

The work reported in this paper is based on the following scheme. First, we carry out accurate estimations of the interaction energy of  $H_2$  adsorbed on graphene, graphdiyne and graphtriyne molecular prototypes. Then, after assessing the most appropriate graphyne for  $H_2$  physisorption, we obtain the equilibrium 3D structure of the related graphyne multilayer. Finally, the  $H_2$  interaction with the proposed novel graphite composed of graphyne layers is also investigated.

## II. COMPUTATIONAL METHODS

The electronic structure calculations for the  $H_2$  adsorption energy have been carried out at the MP2C[21] level of theory by using the Molpro2012.1 package[22]. For the graphene prototype the C-C bond length is 1.42 Å while for the graphyne pores we have considered the following bond lengths[23]: 1.431 Å for the aromatic C-C, 1.231 Å for triple C-C, 1.337 Å for the single C-C between two triple C-C bonds, 1.395 Å for the single C-C connecting aromatic and triple C-C bonds. In all cases the C-H and H-H bond lengths are 1.09 and 0.746 Å, respectively. The aug-cc-pVTZ[24] basis set was employed for the molecular planar structures, while the aug-cc-pVQZ[24] basis has been used for the  $H_2$  molecule. All considered molecular structures are treated as rigid bodies: the atoms composing the investigated graphene and graphynes prototypes are frozen in their initial positions and the molecular configuration of  $H_2$  is not allowed to relax during the calculations. The interaction energies have been further corrected for the basis set superposition error by the counterpoise method of Boys and Bernardi[25].

The calculations for the graphtriyne 3D structure have been obtained by means of density-functional theory (DFT), as implemented in the VASP code [26], within the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE)[27]. The Blöchl all-electron projector-augmented wave (PAW) method [28, 29], with an energy cutoff of 750 eV and a  $2s^2 2p^2$  electron valence potential for carbon, has been employed. A periodic model has been considered with an initial supercell system for the graphtriyne isolated bilayer constituted by 48 C atoms per layer (96 C atoms) with in-plane lattice parameter

$a = 12.035 \text{ \AA}$  and  $b = 20.841 \text{ \AA}$ , and with a sufficient vacuum amount to avoid spurious interaction between bilayers along the direction normal to the  $ab$  plane. According to the large size of the parameters, we have sampled the Brillouin zone with a  $5 \times 4 \times 1$  Gamma centred mesh. Keeping the supercell lattice parameters fixed to the initially optimized values, and similarly keeping fixed the coordinates of the bottom graphdiyne monolayer, by means of single point calculations we have progressively reduced the interlayer distance  $R$  by decreasing the coordinates along  $c$  of the top graphdiyne monolayer.

The computed energies have been corrected by two- and three-body dispersion contributions including the Becke-Johnson damping scheme[30] and an Axilrod-Teller-Muto three-body term[31], as implemented in the *dftd3* program of Grimme et al.[32].

### III. RESULTS AND DISCUSSION

#### A. Single layer adsorption energies

In the upper part of Fig. 1 we report the planar molecular structures that can be considered as the smallest precursors[10, 20] of the graphene plane and of graphdiyne and graphdiyne pores and which are here used as prototypes to study their interaction with the  $H_2$  molecule, shown in red in the center of each structure. In particular the potential curves obtained at the MP2C level of theory and depicted in the lower part of Fig. 1 refer to the  $H_2$  molecule kept parallel to the molecular prototype planes and approaching their geometrical centers. The chosen relative configurations (sketched in the upper part of Fig. 1) are kept frozen during the calculations and are those providing for each case both the deepest interaction well and the lowest repulsive well at short distances. In the case of graphene the minimum is located at about  $2.9 \text{ \AA}$  from the plane and the related well depth is about  $53 \text{ meV}$ . This findings are in very good agreement with previous experimental[14] and theoretical[15, 16] estimations. Moving from graphene to graphynes the corresponding well depth becomes deeper and closer to the carbon plane. In particular for both graphdiyne and graphdiyne a well depth of about  $63 \text{ meV}$  is obtained, while the minimum is found at  $1.8 \text{ \AA}$  for the former and right in the plane for the latter. In order to qualitatively draw conclusions on the possibility of hydrogen intercalation a vertical line, corresponding to the graphite half interlayer distance (equals to  $1.675 \text{ \AA}$ ), is also depicted. At this distance the

potential for graphene is already very repulsive (about 1000 meV) and this clearly confirms that the existence of molecular hydrogen inside graphite is not possible. Nevertheless in the case of the two graphynes a quite different scenario appears: for graphdiyne the minimum almost matches graphite half interlayer distance while for graphtriyne, even if the corresponding well is located at shorter distances, it is actually quite flat and around 1.7 Å the interaction potential is still attractive and around -50 meV. Moreover, the penetration barrier is extremely large for graphene, it becomes quite lower for graphdiyne, and it completely disappears for graphtriyne. Therefore from the results of Fig. 1 it can be inferred that for graphynes not only the adsorption energy seems to be more favourable than for graphene but also that hydrogen out-of-plane diffusion and intercalation could be possible in multi-layer graphynes.

In order to further investigate these possibilities we have studied more in details the features of the  $\text{H}_2$ -graphynes interaction by considering the hydrogen molecule right inside the graphynes' pores. In fact, in Fig. 1 a low but non-negligible penetration barrier has been found for graphdiyne and a better description of its features, which can affect the diffusion of the hydrogen molecule through the pores, is desirable. In Fig. 2 the in-plane behavior of the  $\text{H}_2$ -graphynes interaction is reported. In details, we show the interaction potential as a function of the displacement of the  $\text{H}_2$  molecule from the pore geometric center and along two main directions (see upper part of Fig. 2). First of all we notice that for both graphynes the potential does not depend dramatically on the orientation of the  $\text{H}_2$  molecule: if it is parallel to the pore plane (solid line) then it is slightly more attractive around the geometric center than the profile for the perpendicular configuration (dashed line); on the other hand the opposite occurs when the potential becomes repulsive, that is for displacements in general larger than 1 Å. This behaviour could be expected considering that the  $\text{H}_2$  molecule is almost spherical from the electronic structure point of view since both its quadrupole moment and dipole polarizability anisotropies are small [33]. More importantly, a quite large interaction anisotropy is indeed found for graphdiyne when the  $\text{H}_2$  molecule is out of the geometric center: even for displacements as short as few angstrom tenths in both directions the potential is more than twice and then increase rapidly reaching very repulsive values of about 1000 meV at around 1 Å from the center. Therefore even if for graphdiyne the barrier for  $\text{H}_2$  passage through the pore apparently seems to be low it assumes indeed values below 50 meV just in a very reduced area of about  $0.04 \text{ Å}^2$  around

its center. These findings suggest that the  $\text{H}_2$  diffusion through the graphdiyne pore is very unlikely at standard temperature and pressure. On the contrary, for graphtriyne the in-pore interaction anisotropy is quite lower: we can observe a flat well spreading in both coordinate directions and the potential remains attractive for displacements from the center as large as about 1 Å. These results suggest that for graphtriyne pores there is a large area (about 3 Å<sup>2</sup>) available for an unimpeded  $\text{H}_2$  passage; it follows that one hydrogen molecule can diffuse through the layer and be easily adsorbed in the pore. We can also infer that in principle if a further  $\text{H}_2$  is taken into account both of them can not coexist in the pore plane since the equilibrium distance (about 3.3 Å) for the  $\text{H}_2$  dimer[34] is larger than the diameter of the area describing the attractive potential. Therefore on the basis of the results reported in Figs.1 and 2 we can conclude that graphtriyne sheets are better than graphdiyne ones to build up ideal carbon-based layered surfaces suitable for  $\text{H}_2$  physical adsorption; in fact, the pores of the former provide a large area featuring an attractive interaction potential which also extends out of the plane maintaining negative values lower than -30 meV even for distances as far as 2.5 Å from the layer.

### B. Multi-layer structure and adsorption energies

In order to further investigate the possibility of hydrogen adsorption on graphtriyne surfaces the next convenient step has been to consider a multi-layer to assess whether intercalation is really energetically favorable or not. To do that we have considered a novel kind of graphite which is composed of stacked graphtriyne sheets instead of graphene layers; its actual 3D structure represents a critical point since it could occur that the interlayer distance is too short to allow the hydrogen molecules to be hosted and also that the pore of one layer is partially obstructed by benzenic rings of the adjacent layers.

The 3D arrangement of bulk graphyne and graphdiyne has been recently investigated[18, 35, 36] by means of periodic dispersion-corrected DFT calculations and it has been found that the corresponding interlayer equilibrium distance is likely larger[18, 35] than that of graphite. Nevertheless we believe that the methodologies employed in these studies are not accurate enough to guarantee the reliability of the estimated 3D structure since the reported results in the case of pristine graphite, which is used as a benchmark test, showed that the related interlayer equilibrium distance is not correctly reproduced. Therefore our

choice has been instead to employ for the graphtriyne multi-layers the approach very recently introduced by Brandenburg et al. [37] which provided accurate and reference values for both exfoliation energy and interlayer separation of graphite.

In particular we have considered at first a supercell containing an isolated graphtriyne bilayer (see Fig. 3) and we have assumed that its relative configuration is similar to that of the most stable Bernal stacking found in pristine graphite: benzene rings in different adjacent layers are displaced of 1.431 Å along one of the acetylenic chains joining two contiguous rings. This relative orientation corresponds to a minimum also in the case of bulk graphdiyne[36] and it has been considered frozen throughout the DFT calculations whose results provided the cell energy as a function of the interlayer distance, as shown in Fig. 3. We have found that the equilibrium interlayer distance for the graphtriyne bilayer is 3.45 Å, which is just 0.1 Å larger than that for pristine graphite. This result could be understood considering that a graphtriyne plane contains a lower density of carbon atoms with respect to graphene and consequently the size of both attractive and repulsive contributions to the interlayer interaction is presumably reduced.

Once the structure of the graphtriyne bilayer has been determined we have used the related equilibrium geometry to build up a graphtriyne multilayer prototype. To do that we have considered three parallel graphtriyne pores in a Bernal-like stacking and with adjacent layers separated of 3.45 Å. The used prototype for the graphtriyne trilayer is reported in Fig. 4 and its choice is justified since its reduced size allows the application of the accurate but computationally expensive MP2C level of theory to determine the H<sub>2</sub> adsorption energy. In Fig. 4 the positions of the H<sub>2</sub> molecule considered for the calculations are also reported and they are indicated with A, B, C, B' and A' blue letters. In particular the A, A' and C sites correspond to in-pore configurations in which the H<sub>2</sub> molecule is right in the pore geometric center and parallel to the layers. B and B' equivalent sites correspond instead to the H<sub>2</sub> intercalation: the molecule center of mass lie right in the direction (dashed line) joining the geometric centers of adjacent pores and it is placed at 1.725 Å (half the interlayer distance) from the closest layers, with the diatom oriented parallel to them. The reported adsorption energies obtained at the MP2C level and shown in the lower part of Fig. 4 correspond to the sum of three contributions related to the H<sub>2</sub> molecule interacting with each of the graphtriyne pore. It can be seen that for the in-pore A, A' and C locations the obtained interaction energies are significantly larger than that for the single pore case



(see Figs. 1 and 2): clearly the largest interaction correspond to the C case with the  $H_2$  molecule inside the intermediate pore and the related adsorption energy is about 96 meV. As for the B and B' intercalation sites, the interaction energies are also very attractive, around -90 meV, even if slightly less than that for the C position. The obtained results for the C and B sites should be considered as reliable estimations of typical in-pore and intercalation interaction energies for  $H_2$  inside a periodic graphtriyne multi-layer and their large value, especially considering that only non-covalent interactions are involved, allow to suggest the following conclusions. The first point is that no impediment is present for  $H_2$  penetration across graphtriyne multi-layers since it can pass from a pore to the adjacent one along the  $z$  direction (see Fig. 4) without any barrier. This means that the out-of-plane diffusion through the novel porous graphite is feasible. Nevertheless it should be clarified that in-plane diffusion (i.e. along the directions perpendicular to  $z$ ) is instead very unlikely for the inner layers since the interaction energy becomes very repulsive when  $H_2$  is close to the carbon atoms (see Fig. 2 and Fig. S1 of the Supplementary Material). The second point to highlight is that the quite favourable interaction energies imply that this novel porous carbon material could be used for hydrogen reversible storage.

On the basis of present results we can safely conclude that at least one hydrogen molecule could be stored per graphtriyne pore; if we consider the periodic cell reported in Fig. 3 we can qualitatively estimate gravimetric and volumetric capacities of about 1.4 wt% and 0.015 kg/L<sup>-1</sup>, respectively. Even if these predictions are comparable with the best hydrogen uptakes obtained so far for other carbon nanostructures[38, 39] at room temperature, they are however somehow far from the best target proposed by the DOE[2]. Still, by taking into account that intercalation is also possible, we expect that more than one hydrogen molecules could accommodate themselves above and below each pore. As an example, if we assume that three  $H_2$  molecules can coexist between the parallel openings we could reach gravimetric and volumetric capacities of about 4 wt% and 0.046 kg/L<sup>-1</sup>, respectively, which are in the range or even beyond the wanted storage limits[2].

#### IV. CONCLUSIONS

In summary, by means of electronic structure computations, we have shown that graphynes are more suited than graphene for the physical adsorption of  $H_2$ . As a matter of

fact the adsorption energy on a single layer is larger on graphynes and the  $H_2$  equilibrium distance is closer to the carbon plane. The features of the considered graphynes pores have been further investigated and we have demonstrated that for graphdiyne the in-pore interaction is repulsive and represents a high impediment to  $H_2$  crossing; on the contrary for graphtriyne the in-pore interaction is attractive and a flat minimum is found. On the basis of these results a novel type of graphite, composed of graphtriyne stacked layers, is proposed and its structure is determined. By performing calculations of the interaction energy for the graphtriyne multi-layer we have found that the  $H_2$  molecule can freely diffuse in the direction perpendicular to the carbon sheets and that in-pore and intercalation sites provide very favourable adsorption energies in the range of 0.1 eV.

Present data provide reliable benchmark results that can be used to tune-up a new force field suitable to perform dynamical simulations capable to correctly assess the actual  $H_2$  uptake of this novel material. Work in this direction is in progress.

The proposed porous graphite could be considered as a promising alternative to more traditional adsorbing materials such as zeolites and MOF; in fact it shares with them a crystalline structure with regular pores of well defined size but with the vantage points of being in principles lighter, chemically inert and thermally stable. Hopefully theoretical investigations on this topic can further stimulate the progress in the synthesis of large pore graphynes such as graphtriyne, the building block of the porous graphite here introduced.

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### Supplementary Material

Intermolecular potentials related to different configurations used for graphtriyne pore- $H_2$  computations are reported in an additional figure. This information is available free of

charge via the Internet.

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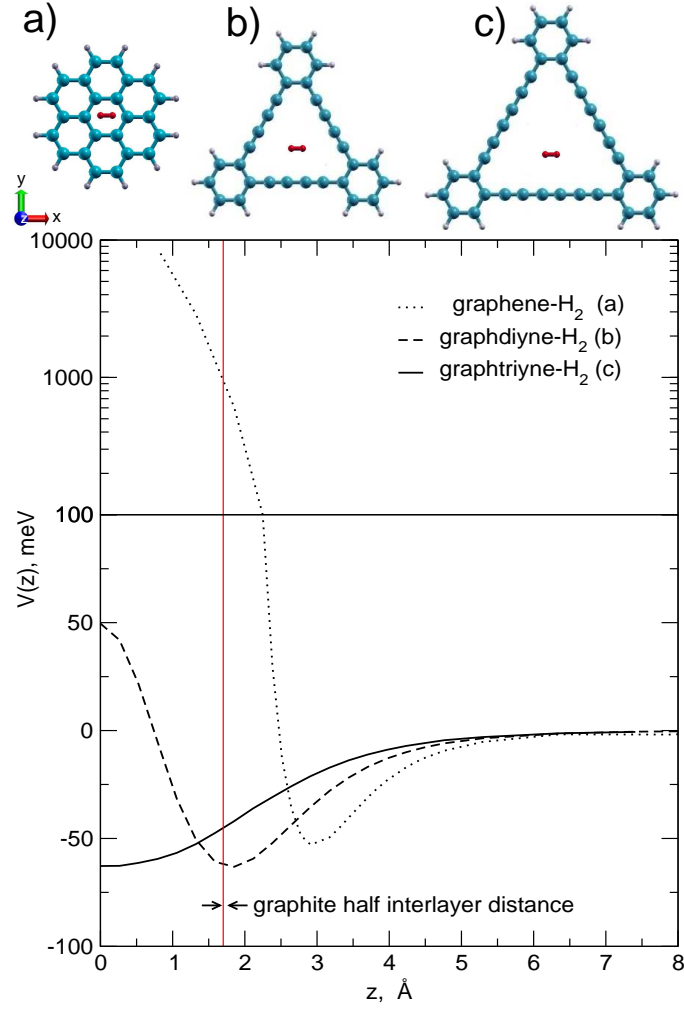


FIG. 1: Upper part: planar molecular prototypes used to study the graphene plane (a) and the pores of graphdiyne (b) and graphtriyne (c); they are known as coronene, dodecadehydrotribenzo[18]annulene and octadecadehydrotribenzo[24]annulene, respectively. The H<sub>2</sub> molecule is shown in red, and its center of mass coincides in each case with the geometric center of the coronene and annulenes; their relative distance is indicated as  $z$ . Lower part: adsorption energy profiles obtained at the MP2C level of theory for H<sub>2</sub> approaching the geometric center of the planar molecular prototypes and kept parallel to them. The vertical red line placed at 1.675 Å corresponds to the graphite half interlayer distance.

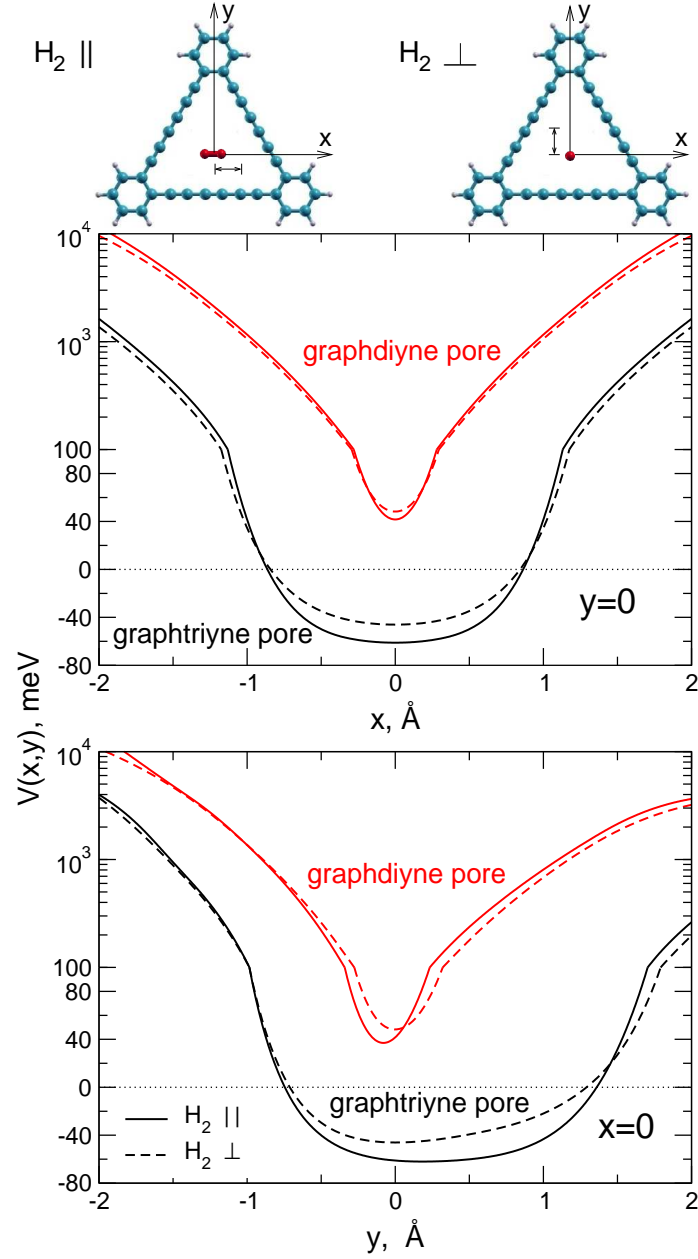


FIG. 2: In-plane behavior of the  $H_2$ -graphdiyne (red curves) and  $H_2$ -graphtriyne (black curves) interactions as functions of the  $H_2$  displacements ( $x$  and  $y$ ) from the geometric center of the pores. Two different  $H_2$  orientations are considered, namely parallel (solid lines) and perpendicular (dashed lines) to the annulenes' planes. The black double-headed arrows shown inside the triangular pores roughly describe a linear distance of about 2 Å in the  $x$  or  $y$  directions. Upper panel:  $y$  is kept equals to 0 while  $x$  may vary. Lower panel:  $x$  is kept equals to 0 while  $y$  may vary.

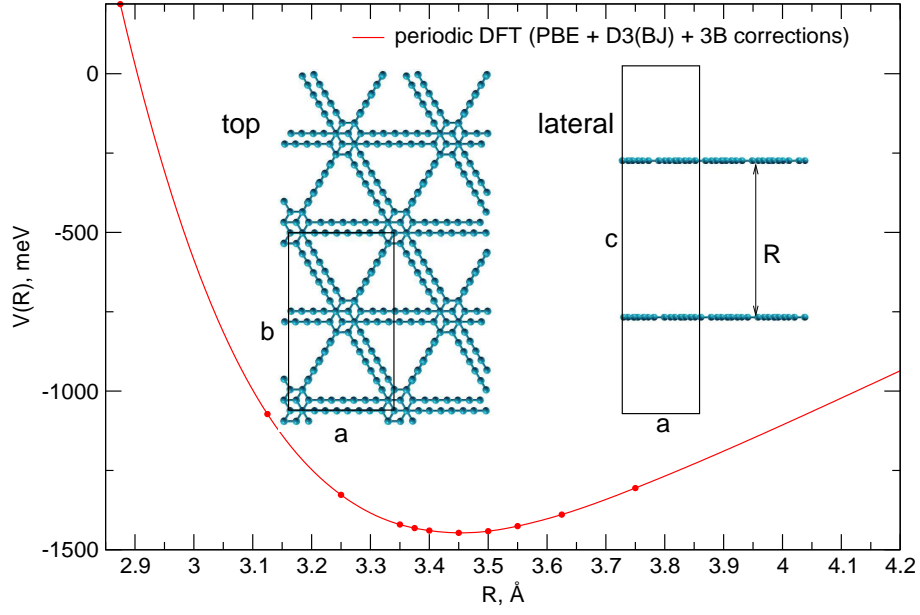


FIG. 3: Top and lateral view of the supercell describing the graphtriyne bilayer used in the periodic DFT calculations;  $a$ ,  $b$  and  $c$  lattice parameters are also reported and throughout the calculations they are kept frozen while the interlayer distance  $R$  is varied. The DFT cell energies (relative to the asymptotic layer separation) are properly corrected by an “a posteriori” dispersion correction which take into account for the Becke-Johnson (BJ) damping scheme and three-body contributions (3B) and then depicted as a function of  $R$ .

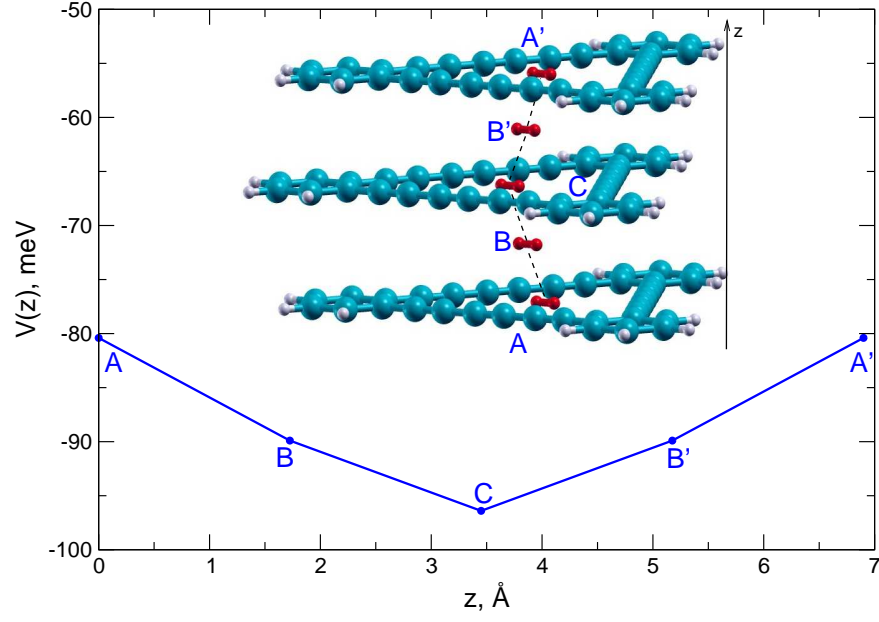


FIG. 4: Interaction energy evolution of one  $\text{H}_2$  molecule crossing a porous graphite composed of stacked graphtriyne layers. A prototype consisting of three parallel graphtriyne pores in a Bernal-like 3D arrangement is used. The A, A', B, B' and C letters indicate different adsorption sites of the  $\text{H}_2$  molecule: A, A' and C locations correspond to in-pore configurations while B and B' sites to intercalation equivalent positions. The five adsorption sites lie on the dashed lines which join the geometric centers of adjacent pores and the layers separation is fixed at 3.45 Å, the equilibrium distance provided by the calculations shown in Fig. 3.